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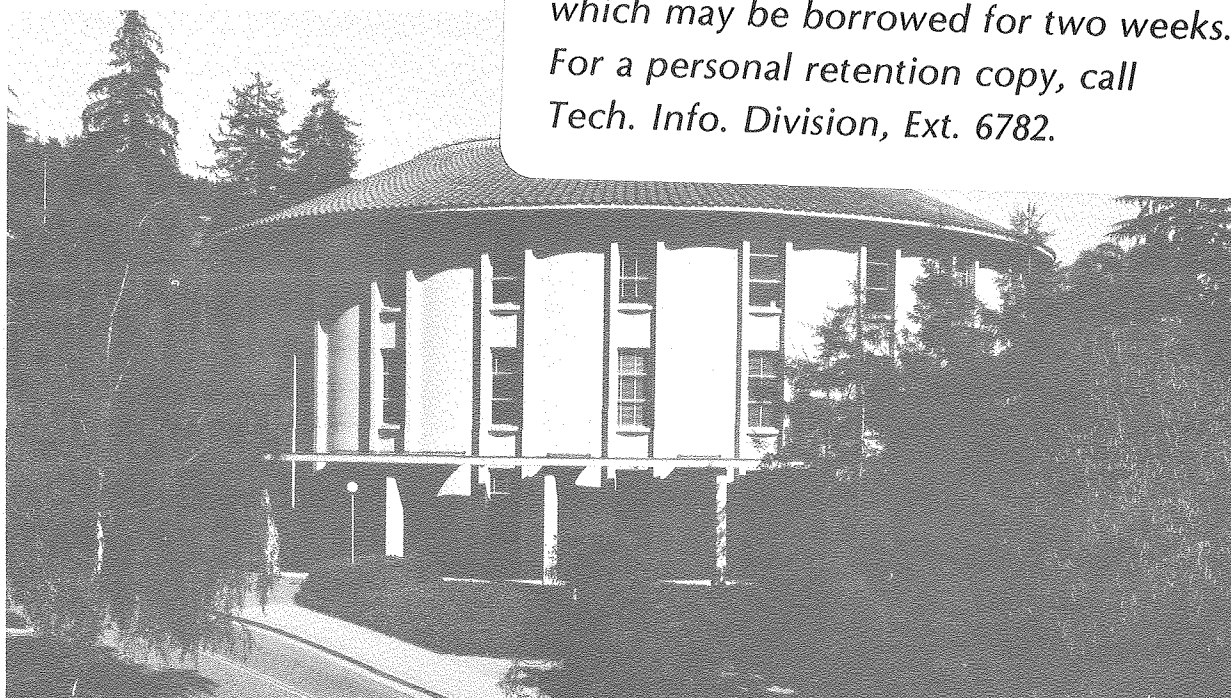
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Effect of longitudinally polarized protons on
optically active amino acids

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As a test of the Vester-Ulbricht hypothesis that the specific optical activity of contemporary biology arose from a differential action of polarized nuclear particles, DL-leucine has been irradiated with protons of both positive and negative longitudinal polarization. Neither kind of protons caused any measurable decomposition difference in the two amino acid optical isomers of the amino acid.

Many efforts have been made¹ to find an experimental demonstration of the hypothesis of Vester and Ulbricht² to explain the fact that protein amino acids are (with some minor exceptions in bacteria) entirely formed from the L-optical isomers. This hypothesis postulates that the excess of "anti-parallel" polarized beta particles from natural radionuclides, i.e., parity violation, gave a slight preference for the genesis of L-amino acids over D-amino acids on the prebiological Earth. This preference would arise from the betas' interactions in such a way as to selectively favor the formation of L-amino acids and/or promote the selective decomposition of D-amino acids.

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Experimental work on the Vester-Ulbricht (V-U) hypothesis has included studies on a great variety of optically active organic compounds that have been irradiated with betas³⁻⁷ and positrons^{8,9} from radionuclides, and with accelerated, polarized electrons^{10,11} and muons¹². The results have been mixed, but it can be said at once that no report of a claimed selective optical isomer-polarized particle interaction has been successfully duplicated in another laboratory. The V-U hypothesis is still considered a reasonable one, but, without doubt, it still lacks experimental reproducible confirmation.

Another promising approach to test the V-U hypothesis is through the use of polarized protons. Such protons are available with the equipment recently installed on the Lawrence Berkeley Laboratory's 88-inch, sector-focused cyclotron. The polarized beam from the cyclotron has its spin-polarization axis aligned along the cyclotron magnetic field direction (vertical). The external beam first passes along the axis of a solenoid magnetic field, which precesses the spin direction through 90° into the horizontal plane, although still transverse to the beam direction. A dipole magnet then bends the beam through an angle of 47.7°, and, at the same time, precesses the spin axis into the beam direction. Thus, the vertical polarization (up or down) of the proton beam from the cyclotron is converted to longitudinal polarization (positive is in the direction of the beam's propagation, and negative is in the reverse direction). The beams incident upon the samples were typically of about 10 MeV and were limited to 10-14 nanoamps. The degree of polarization for both proton spin directions was approximately 80%.

The potential advantages in the use of protons in the search for an asymmetric effect in their interactions with matter are as follows:

- (1) The protons, like the muons that have been used in similar experiments¹², have a higher degree of polarization (80%) than those reported for polarized electrons (10-47%)^{10,11}.
- (2) The protons are slower moving than any other particles previously employed in the search for asymmetric effects that might produce optically active compounds. For example, as can be seen from the following equations, at a given kinetic energy the protons will move at a velocity of about 1/45 that of the electrons:

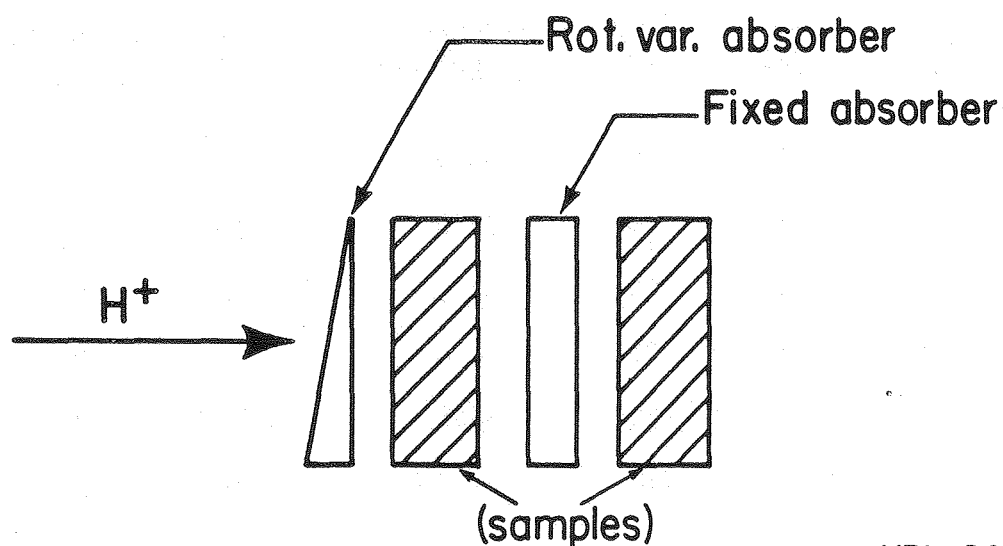
$$\begin{aligned} \text{K.E.} &= \frac{1}{2} m v^2 \\ \frac{v(e^-)}{v(H^+)} &= \frac{\sqrt{(1/2)(1)}}{\sqrt{(1/2)(5 \times 10^{-4})}} \end{aligned}$$

The slower velocity of the proton should maximize the time for interactions between the polarized protons and the electrons of an optically active molecule. The protons in the experiments reported here interacted at all kinetic energies from about 10 MeV down to zero.

- (3) The ionization density along the proton's track will be much greater than along the track of a lighter particle such as an electron. This will be particularly true at the "Bragg peak" at the end of the particle's track.

We have carried out six irradiations with polarized protons. Each irradiation was done on a pair of DL-leucine disks, each about 1 cm in diameter, about 0.1 cm thick, and weighing 110-130 mg. Leucine was the amino acid of choice because it gives an excellent separation of its D- and L-optical isomers on the optically active gas chromatographic column described below. The disks (pressed wafers) were mounted with respect to the proton beam as shown in Fig. 1.

Longitudinally-polarized H^+ Irradiations (0-11 MeV)



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Fig. 1. Schematic for the leucine irradiations. The protons approach from the left, passing successively through a rotating Al absorber, Leu sample, a fixed absorber, and another Leu sample. The rotating and fixed absorbers are designed so that each sample receives an approximately uniformly distributed dose, and the absorber thicknesses are such as to permit the protons to pass entirely through the first sample and stop in the second. The beam incident on the first sample has an energy of 9.5-12.7 MeV. The loss of energy is about equal ($5 \text{ MeV}/H^+$) in each sample.

The principal experimental conditions for the four irradiations are given in Table 1.

Table 1. Experimental conditions for the irradiation of DL-leucine with longitudinally polarized protons

<u>Expt.</u>	<u>Spin</u>	<u>Av. namps</u>	<u>Time min.</u>	<u>Integrated μcoulombs</u>	<u>Approx. rads*</u>	<u>Approx. % Decomp. [†]</u>
1	-	11.5	30	18.0	1×10^8	7
2	+	10.5	114	72.0	4×10^8	25
3	-	13.0	80	57.1	3×10^8	20
4	+	14.0	75	62.0	3×10^8	20
5	-	11.0	225	148.5	8×10^8	47
6	+	13.5	195	158.0	9×10^8	50

$$*\text{Rads} = \frac{(\text{coulombs})(6.3 \times 10^{12} \text{ H}^+ \text{ coulomb})(5.5 \times 10^6 \text{ eV/H}^+)}{1}$$

[†]In experiments 1-4 these were determined by amino acid analyzer; in expts. 5 and 6 by the enantiomeric marker technique¹³.

At the conclusion of each irradiation, the leucine samples were dissolved immediately in 2 ml of a warm (about 80°C) solution of 2-propanol that was saturated with HCl gas. Their subsequent conversion to the N-trifluoroacetyl 2-propyl esters, and the gas chromatography (GLC) of these derivatives on an optically-active adsorbant (N-docosanoyl-L-valyl-t-butylamide) were carried out as recently described¹³. This same analytical procedure, when applied to control samples of the unirradiated DL-leucine, showed an enantiomeric composition of $50.14 \pm 0.13\%$ of the D, and $49.86 \pm 0.10\%$ of the L isomer. The GLC procedure gives results whose reproducibility is expected to be within $\pm 0.2\%$. The GLC analyses of the irradiated samples are shown in Table 2.

Table 2. Percent of optical isomers remaining in DL-leucine
irradiated with longitudinally polarized protons

Expt.	Beam ^a	% D	% L	(+) ^f
1	A	50.12	49.88	-
	PT	49.99	50.01	-
2	A	50.14 ^b	49.86 ^b	0.04
	PT	50.01 ^c	49.99 ^c	0.13
3	A	50.11	49.89	-
	PT	50.12	49.88	-
4	A	50.20 ^b	49.80 ^b	0.11
	PT	50.20 ^d	49.80 ^d	0.14
5	A	49.98 ^d	50.02 ^d	0.11
	PT	49.96 ^d	50.04 ^d	0.15
6	A	50.23 ^e	49.77 ^e	0.19
	PT	50.12 ^d	49.88 ^d	0.06

a A = beam absorbed in sample, PT = beam passed through sample

b Average of 2 GLC analyses

c " " 4 " "

d " " 3 " "

e " " 7 " "

f Standard deviation of replicate analyses

It is apparent from Table 2 that we have not detected any asymmetric degradation of DL-leucine with longitudinally polarized protons even at 50% gross degradation. However, in addition to the above discussed potential advantages of using protons in such experiments, there is also a disadvantage. The magnetic moment of the proton is only about 1.5×10^{-3} that of the electron¹⁴. The spin-spin interaction between the polarized proton or electron, on the one hand, and the electrons of a chiral molecule, on the other, would therefore be much smaller in the case of the proton. Perhaps this proton disadvantage overcomes the advantages of higher polarization, lower velocity, and higher ion densities.

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